

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of:  
First named inventor  
Kilaas, Lars

Application No.: 10/519,167

Filing Date: March 21, 2006

For: Binding a Target Substance

Art Unit: 1641

Examiner: Do, Pensee T

Attorney Ref. No.: 860144.401USPC

Confirmation No.: 5279

**DECLARATION UNDER 37 C.F.R. § 1.132**

**Mail Stop Amendment**  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

1.1 I, Lars Kilaas, hereby declare and state as follows: I am a citizen of NORWAY residing at Skansegt. 17 C, 7014, Trondheim.

**Background**

2.1 I confirm that I am an inventor of the subject matter claimed in 10/519,167. I am currently a Project Director at Sinvent AS of Trondheim, Norway.

2.2 I have read and am thoroughly familiar with the specification and claims relating to the above-identified patent application.

2.3 An accurate copy of my Curriculum Vitae detailing my education and employment experience is filed herewith.

Claim rejections under 35 USC § 102

3.1 I have read and am thoroughly familiar with the Examiner's claim rejections under 35 USC § 102 as set out in the Office Action issued by the United States Patent and Trademark Office on November 13, 2009.

3.2 In addition, I have read and am thoroughly familiar with the documents Weitschies et al. (US 6,027,946), Tan et al. (US 6,548,264) and Rohr (US 5,445,970) as cited by the Examiner in the Office Action.

3.3 I confirm that the magnetic properties of magnetic materials depend on the type (composition) of material, synthesis of material and in particular the size of the magnetic crystals formed during the precipitation process. Both ferromagnetic and ferrimagnetic materials (magnetite) may show both superparamagnetic and remanence behavior. Depending on the sizes of the ferromagnetic crystals, the materials having particle size typically in the range of 10 – 50 nm (single domain crystals) will have superparamagnetic characteristics (essentially no hysteresis or residual magnetization after removal of an applied external magnetic field), while larger crystals (multiple domains) will have residual magnetization after a magnetic field is removed (remanence). The relaxation time for magnetic moments within a domain which are randomly oriented is thus size dependant. This particle diameter, often referred to as "the critical superparamagnetic size",  $D_p$ , is describe in several publications e.g. Toshihiko Sato et. al. "Journal of Magnetism and Magnetic Materials 65 (1987), p. 252-256. Size dependency is also described by Massart, R., US Patent 4,329,241 (1982) and Cullity, B.D., "Introduction to Magnetic Materials, Addison-Wesley, 1972, pages 383-391 (and in particular pages 386-387) and pages 410-416 (and in particular pages 414-415). Single domain crystals are explained in: <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/ferro.html>. Hence magnetite  $Fe_3O_4$  can be produced as an essential (and practical) superparamagnetic and a ferromagnetic material.

3.4 Further, I confirm that remanent materials are different from superparamagnetic materials. The difference in material properties is due to the material's ability to "remember" a magnetic moment after being exposed in a magnetic field. These properties are explained in 3.3 above. The same starting materials can be used to produce these two types of magnetic materials, but the procedure and molar composition of reagents will determine the properties of the final product.

3.5 Accordingly, I confirm that the simple disclosure in a document of a ferromagnetic material, a ferrimagnetic material, an iron oxide material, or magnetite, may refer to materials that do not exhibit remanence. Based on the state of the art, as discussed in 3.6 below, one of ordinary skill in the art would not understand such a listing of materials to be a disclosure of magnetic materials exhibiting remanence.

3.6 I confirm that to the best of my knowledge, at the priority date of the present invention, i.e. 1<sup>st</sup> July 2002, it was the general view in the art that magnetic particles for the purpose of binding target substances, as part of a method of detection or separation, should not exhibit remanence. In particular, as discussed in the third paragraph on page 3 of the application as originally filed, it was thought that remanent particles are undesirable because they disadvantageously form aggregates because of their remanence. It was thought that these aggregates prevent intimate mixture with the sample containing the target substances, and were therefore considered to inhibit partially binding of the target substance with the particles.

Weitschies et al.

4.1 In relation to the disclosure of Weitschies et al. I note from column 2, lines 43 to column 4, line 45, that this document relates to the qualitative and/or quantitative detection of target molecule using a method comprising the steps of a) applying magnetic particles in order to bind target molecules, and form a magnetic complex (MC), b) applying a external magnetic field and

c) turning off the magnetic field and measuring the relaxation time of the MC. Calibration of the system using different loading of the target molecules, makes it possible to do quantitative measurements of unknown samples.

4.2 My understanding of the method of Weitschies et al. is that it requires the use of magnetic material which exhibits relaxation of magnetization over the period of the method. Thus the method needs to be performed with superparamagnetic materials, which are capable of such relaxation. Hence the preferred properties described in this patent teach superparamagnetic particles and the person of ordinary skill in the art would not be taught to use remanent magnetic material.

4.3 Further, my understanding of the particles disclosed in the Examples of Weitschies et al. (column 9, example 1) is that these are superparamagnetic because all examples are based on superparamagnetic particles produced according to example 1. Example 1 states that the dextran-coated magnetic material is bought from Meito Sangyo. From their website ([http://www5.mediagalaxy.co.jp/meito/kaseihin/index\\_e.html](http://www5.mediagalaxy.co.jp/meito/kaseihin/index_e.html)) - under Dextran derivatives / FERUCARBOTRAN (magnetic iron oxide-dextran complex) - the Meito company states that these particles are superparamagnetic, and hence the particles produced in all the rest examples are thus superparamagnetic.

4.4 I also note that Weitschies et al. discloses the need for the colloidal suspensions to be "freely moveable ferromagnetic or ferromagnetic particles" (column 6, lines 13 to 15). This also supports the view that Weitschies et al. are not teaching the use of remanent particles because remanent particles aggregate in a liquid phase and as such are not "freely moveable".

Tan et al

5.1 In relation to the disclosure by Tan et al., I note that this document discloses a large number of different nanoparticle types for a vast array of uses (column 2, lines 10 to 15). Tan et al., discloses that in some variations the nanoparticle cores can be magnetic (column 2, lines 27 to 30). Further, the document teaches that the type of core should be selected based on the intended application (column 5, lines 1 and 2). I note that particles having remanent magnetization are only mentioned in the context of particles which are useful in binary magnetic recording applications (column 12, third paragraph). Such a use, i.e. binary data storage is clearly different from the use of the magnetic particles of the present invention, which are designed for use in a liquid phase in the binding of a target substance, to allow the substance to be separated from a sample. Magnetic particles for binary magnetic recording applications, such as those disclosed in Tan et al., may not be "capable of binding a target substance" according to the present application, and in particular may not be capable of binding a nucleic acid. Further, there is no indication that the remanent particles of Tan et al., would have the functional groups necessary to promote disaggregation in a liquid phase.

5.2 In particular, I note that in the Examples magnetic nanoparticles are described. I confirm that the procedure described for the production of these particles is a procedure which generates superparamagnetic materials (ferrofluids). In all the described examples the magnetite formed is based on precipitation of a mixture of  $Fe_2$  and  $Fe_3$  ions. This is in general the common published process for making superparamagnetic ferrofluids, having oxide sizes in the low nanometer range (5-30 nm). The size of the oxide formed when mixing the solution containing iron ions (Example 1, first container) with the  $NH_4OH/AOT$  solution (Example 1, container 2) will essentially be the same (due to stoichiometric composition of reagents) regardless the size of the micelles or droplets that undergo coalescence. The later formed core made up by multiple superparamagnetic oxide (ferrofluid) will remain superparamagnetic.

Rohr

6.1 In relation to the disclosure of Rohr I note that this document discloses a magnetically-attractable material as a detectable label in binding assays. As explained in column 2 lines 45 to 58, the magnetic label is subjected to a magnetic field and the label displays a resultant force or movement. The extent of the force or movement is modulated by an analyte that may be present in the test sample. The effect of the magnetic field on the magnetically-attractable label can be used as a measure of the presence or amount of an analyte in a test sample. Accordingly, I believe that it is apparent to persons skilled in the art that this method works in a manner similar to that of Weitschies et al, described above.

6.2 I note that in the examples only superparamagnetic particles are described and thus I consider that the person of skill in the art would be deterred from using magnetic materials that exhibit remanence, especially when considering the general view of the state of the art as discussed in 3.6 above. Indeed, one of ordinary skill in the art would be led towards using superparamagnetic material when working the method described in this document.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that all statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents ensuing thereon.

Respectfully submitted,

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## MAGNETIC PROPERTIES OF ULTRAFINE FERRITE PARTICLES

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The morphology and magnetic properties of ultrafine ferrite particles prepared by coprecipitation are studied. Saturation magnetization is found to decrease sharply when the particle size is reduced below 10 nm, and this decrease is found to be related to the crystalline magnetic anisotropy constant  $K_1$ .

## 1. Introduction

Ultrafine  $\text{Fe}_3\text{O}_4$  particles used for magnetic fluids exhibit rather low saturation magnetization (30–60 emu/g) compared to that of bulk material (92 emu/g) [1]. In recent years, several papers have been published on the decrease in saturation magnetization that occurs when particle size is decreased below 20 to 30 nm [2,3]. This paper presents results of studies on the morphology and magnetic properties of ultrafine  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$  and other ferrites with different crystalline magnetic anisotropy constants  $K_1$ .

## 2. Experimental methods

$\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$  and other ferrites were prepared by coprecipitation [4].

The following procedure was used:

- Mixed solutions of 0.1 mol/l of  $\text{MCl}_2$  ( $\text{M} = \text{Fe, Co, Mn, etc.}$ ) and 0.2 mol/l of  $\text{FeCl}_3$  were prepared for single ferrites.
- A 3 mol/l  $\text{NaOH}$  solution was added to the above until the pH reached 13.
- The solutions were boiled for either 30 or 60 minutes at  $100^\circ\text{C}$ . Coprecipitated ferrites were produced.
- The products were filtered, washed with deionized water and dried in 0.1 Torr at  $60^\circ\text{C}$ .

The ferrites were then examined by chemical analysis, X-ray diffraction (XD), electron diffrac-

tion (ED), and transmission electron microscopy (TEM).

The average particle size,  $D_{311}$ , was determined by Scherrer's formula using the half-maximum width of the (311) X-ray diffraction line. The specimens were also placed on a microgrid, and their morphological properties were observed by TEM. Magnetization was measured at room temperature in a vibrating sample magnetometer up to a field of 14 kOe. Saturation magnetization  $\sigma_s$  was estimated by extrapolating to an infinite magnetic field in a plot of magnetization  $\sigma$  versus  $1/H$ .

## 3. Experimental results and discussion

## 3.1. Composition and crystal structure

Various properties of several ferrites are listed in table 1. The composition of the ultrafine ferrites prepared in this study was nearly equal to the stoichiometric values of the bulk ferrites except for ferrites containing  $\text{Fe}^{2+}$  and  $\text{NiFe}_2\text{O}_4$ . Chemical analyses revealed that the rest accounted for approximately 10% of the weight of 5 nm particles and only a small percentage of the weight of 10 nm particles. The rest is considered to be adsorption water on the surface of particles, determined by the measurement of endthermo dip at about  $100^\circ\text{C}$  using a differential scanning calorimetry (DSC) meter.

Lattice constants measured by XD were almost



Table 1  
Various properties of ultrafine ferrite particles

Ferrite	Particle size $D_{311}$ (nm)	Composition MO/Fe <sub>2</sub> O <sub>3</sub> (mol%)	Lattice constant $a_0$ (nm)		Magnetic properties		
			exp.	ASTM	$H_c$ (Oe)		$ K_1 ^c$ (erg/cm <sup>3</sup> )
Co <sub>0.7</sub> Fe <sub>0.3</sub> Fe <sub>2</sub> O <sub>4</sub>	12	35:3:62	0.841	—	330	—	$3.4 \times 10^5$
CoFe <sub>2</sub> O <sub>4</sub>	17	49:51	0.840	—	670	—	$1.8 \times 10^5$
	11	48:52	0.838	0.838	330	$\approx 5100$	
Fe <sub>3</sub> O <sub>4</sub>	17	12:88	0.839	—	$\leq 50$	250	$1.4 \times 10^5$
	15	13:87	0.839	0.840	$\leq 50$	—	
	11	8:92	0.839	—	$\leq 50$	$\approx 150$	
MnFe <sub>2</sub> O <sub>4</sub>	12	48:52	0.848	0.850	$\approx 0$	$\approx 0$	$3.3 \times 10^4$
NiFe <sub>2</sub> O <sub>4</sub>	19 <sup>a</sup>	45:55	0.835	0.834	$\approx 0$	$\approx 0$	$3.3 \times 10^4$
ZnFe <sub>2</sub> O <sub>4</sub>	5	49:51	0.847	0.843	$\approx 0$	$\approx 0$	—
Ni <sub>0.3</sub> Zn <sub>0.7</sub> Fe <sub>2</sub> O <sub>4</sub>	8	14:34:52	0.846	0.840	$\approx 0$	$\approx 0$	$(3 \times 10^3)^d$

<sup>a</sup> After heat treatment at 700°C, 1 h. <sup>b</sup> After E.W. Gorter, Proc. I.R.E. (1955) p. 1945. <sup>c</sup> After R.M. Bozorth et al., Phys. Rev. 99 (1955) 1788. <sup>d</sup> Estimated value.

the same as ASTM card values. As for Fe<sub>3</sub>O<sub>4</sub>, the measured lattice constant of 0.839 nm differed from that of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and spectra corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or Fe(OH)<sub>2</sub> were not observed in X-ray diffraction lines.

The ferrite particles obtained in this study produced defect-free lattice images, and electron diffraction patterns corresponded to a spinel structure. TEM micrographs of CoFe<sub>2</sub>O<sub>4</sub> and Ni<sub>0.3</sub>Zn<sub>0.7</sub>Fe<sub>2</sub>O<sub>4</sub> particles are shown in fig. 1. In fig. 1a, obtained  $d$ -spacings of 0.486 and 0.252 nm in CoFe<sub>2</sub>O<sub>4</sub> particles a and b corresponded to the (111) and (311) of the spinel structure. Edge lines of ZnFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, Ni<sub>0.3</sub>Zn<sub>0.7</sub>Fe<sub>2</sub>O<sub>4</sub> (fig. 1b), and MnFe<sub>2</sub>O<sub>4</sub> are clearly shown, while those of CoFe<sub>2</sub>O<sub>4</sub> (fig. 1a) and Fe<sub>3</sub>O<sub>4</sub> are unclear.

The good dispersion of CoFe<sub>2</sub>O<sub>4</sub> particles into the alkaline solvent, at a pH of about 3, was obtained, as shown in fig. 1c. Estimated particle size was almost 10 nm in diameter.

It was seen from further study that these ferrite particles were idiomorphic even below 20 nm.

## 2. The dependence of saturation magnetization on particle size

The relation between relative saturation magnetization  $\sigma_s/\sigma_{\text{bulk}}$  and particle size  $D_{311}$  is shown in fig. 2 for several ferrites. Here,  $\sigma_{\text{bulk}}$  is the saturation magnetization of bulk ferrites having the same chemical compositions;  $\sigma_s/\sigma_{\text{bulk}}$  has been corrected for the adsorption water content already mentioned.

The superparamagnetic critical size  $D_p$  of each ferrite was estimated from the equation,  $KV \approx 25 kT$ . Calculated  $D_p$  values for CoFe<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub> were about 14, 25 and 50 nm, respectively. Therefore, a large number of these ferrite particles seemed to exhibit superparamagnetic behavior.

Hence, the measured values of coercive force  $H_c$  of several ferrites indicated that Co<sub>0.7</sub>Fe<sub>0.3</sub>Fe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> were consisted of the mixture of ferrimagnetic and superparamagnetic particles, while MnFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and Ni<sub>0.3</sub>Zn<sub>0.7</sub>Fe<sub>2</sub>O<sub>4</sub> were consisted of superparamagnetic particles only even at 77 K, as shown in table 1.

For each ferrite,  $\sigma_s/\sigma_{\text{bulk}}$  was found to decrease with decreasing particle size. The decrease is gradual in the range of 50 to 15 nm, and rather sharp below 15 nm.

Also,  $\sigma_s/\sigma_{\text{bulk}}$  largely depends on the  $K_1$  value for each particle size. If, for equal particle sizes, we compare  $\sigma_s/\sigma_{\text{bulk}}$  for the different ferrites, we can observe that the relative loss in magnetization is larger for materials with a low  $K_1$ , and smaller for materials with a large  $K_1$ , as shown in fig. 3.

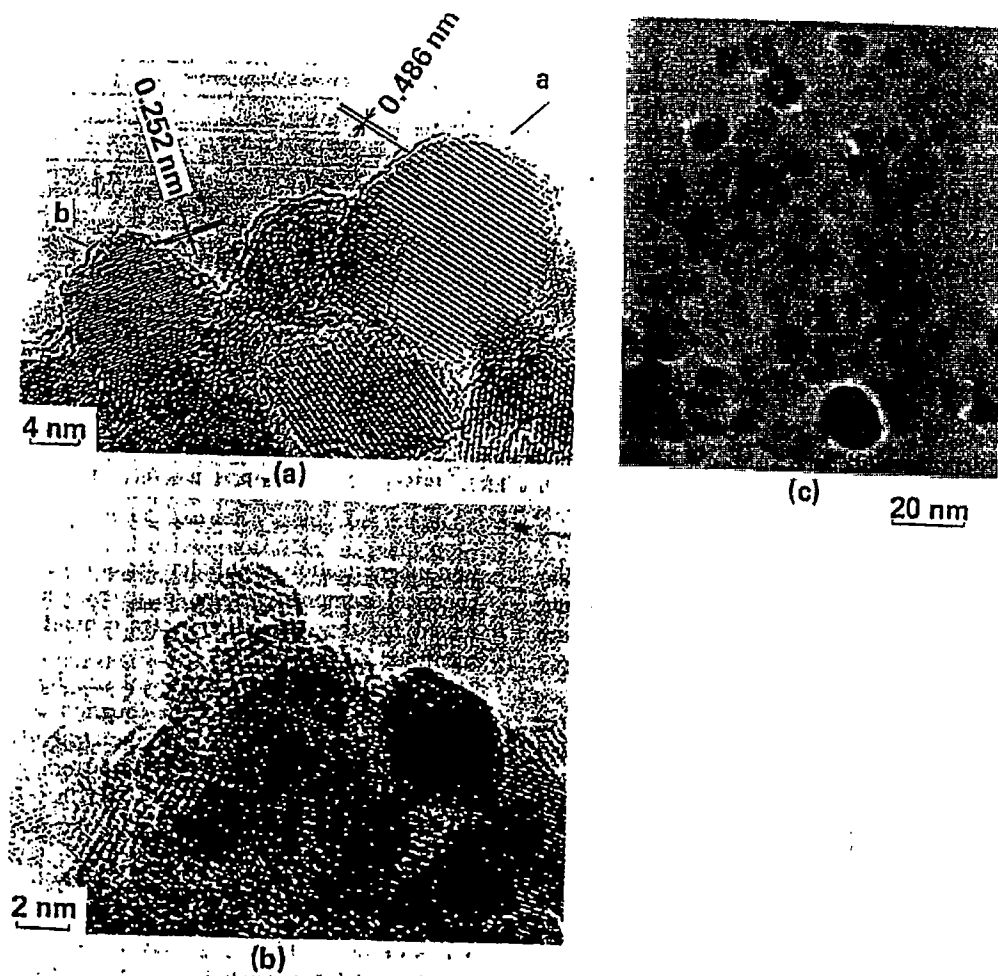


Fig. 1. TEM micrographs of ultrafine ferrite particles. (a) Aggregates of  $\text{CoFe}_2\text{O}_4$ ; (b) aggregates of  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ ; (c) dispersed  $\text{CoFe}_2\text{O}_4$  particles.

### 3.3. The causes of the magnetization decrease

There are several possible causes of the decrease in  $\sigma_s$ : 1) crystal lattice defects, 2) the mass effect of adsorption water on the particle surface, 3) chemical changes on the surface, and 4) magnetic degradation of the surface.

Based on the clear lattice images and XD or chemical analysis, possibilities 1) and 3) may have little effect and can be ruled out. Possibility 2) was

also deleted because these values were compensated, as mentioned above.

Therefore, the decrease in  $\sigma_s$  is thought to be caused by some surface characteristics, such as a magnetically inactive layer or magnetic effect caused by the asymmetric environment of the atoms near the surface.

Assuming a magnetically inactive layer on the particle surface, and considering volume dependencies only, it was estimated that the inactive layer

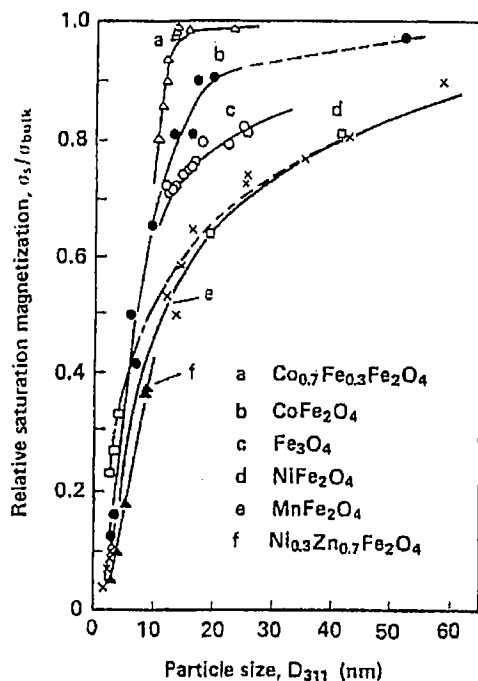


Fig. 2. Dependence of saturation magnetization ratio  $\sigma_s/\sigma_{\text{bulk}}$  on average particle size  $D_{311}$ . Solid line: particles by coprecipitation; broken line: grown particles by heat treatment.

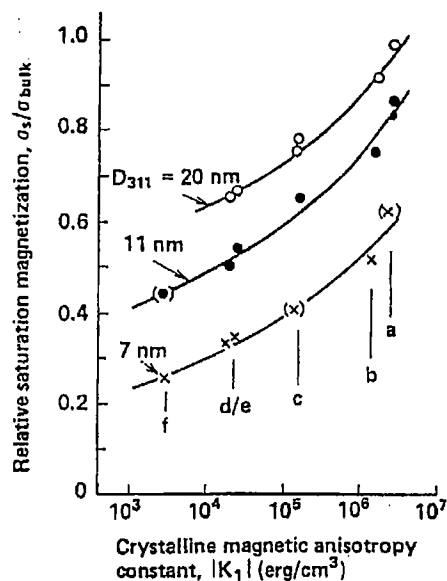


Fig. 3. Relationship between  $\sigma_s/\sigma_{\text{bulk}}$  and  $K_1$  at constant particle size for several different ferrites. Points of a to f indicate materials corresponding to those of fig. 2, and ( ) indicates estimated values.

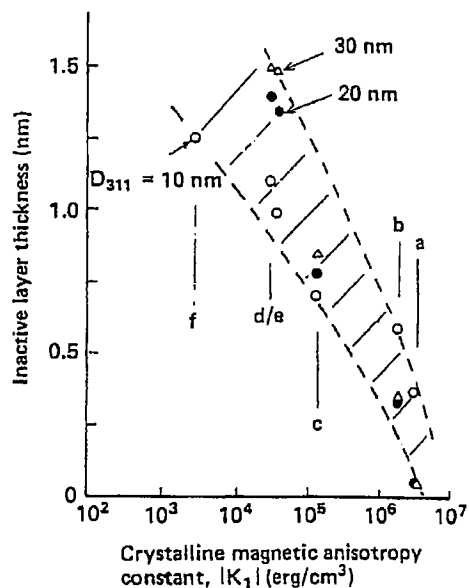


Fig. 4. Relation between magnetically inactive layer thickness and  $K_1$ .

thicknesses correspond to the experimental values of magnetization deficiency. The relation between the inactive layer thickness and  $K_1$  is shown in fig. 4. The inactive layer is estimated to be about 1 nm thick for 10 nm  $\text{MnFe}_2\text{O}_4$ , which has a relatively small  $K_1$ , and 0.4 nm thick for 10 nm  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_{0.7}\text{Fe}_{0.3}\text{Fe}_2\text{O}_4$  particles, which have larger  $K_1$ .

Further study is required to determine the precise origin of the inactive layer.

#### 4. Conclusion

Morphology and Magnetic properties were studied for ultrafine ferrite particles prepared by coprecipitation. A sharp decrease in the relative saturation magnetization  $\sigma_s/\sigma_{\text{bulk}}$  was seen for particles smaller than 10 nm in diameter. Satura-

tion magnetization decreases for all particle sizes were seen to be closely related to crystalline magnetic anisotropy constant  $K_1$ . Sharp decreases in saturation magnetization were attributed to surface effects such as a magnetically inactive layer.

### References

- [1] J. Shimoizaka et al., *J. Japan. Soc. of Powder and Powder Metallurgy* 22 (1975) (in Japanese).
- [2] A.E. Berkowitz et al., *IEEE Trans. Magn.* MAG-16 (1980) 184.
- [3] K. Haneda et al., *J. Japan. Soc. of Powder and Powder Metallurgy* 30 (1983) (in Japanese).
- [4] T. Sato, *IEEE Trans. Magn.* MAG-6 (1970) 795.

[54] **MAGNETIC FLUIDS AND PROCESS FOR OBTAINING THEM**

[75] Inventor: **René Massart**, Cesson, France

[73] Assignee: **Agence Nationale de Valorisation de la Recherche (ANVAR)**, Paris, France

[21] Appl. No.: **168,256**

[22] Filed: **Jul. 10, 1980**

[30] **Foreign Application Priority Data**

Jul. 20, 1979 [FR] France ..... 79 18842

[51] Int. Cl.<sup>3</sup> ..... **G01N 27/82; H01F 1/00**

[52] U.S. Cl. .... **252/62.52**

[58] Field of Search ..... **252/62.51 R, 62.52**

[56] **References Cited**

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Ronay, IBM Tech. Disclosure Bull. vol. 19, No. 7, pp. 2753-2758 (12/76).

*Primary Examiner*—F. Edmundson  
*Attorney, Agent, or Firm*—Hammond & Littell,  
Weissenberger and Muserlian

[57] **ABSTRACT**

New ferrofluids.

They consist essentially of an aqueous sol of polyoxyanions of Fe(III) and at least one metal of oxidation degree II from the first series of transition metals, with an associated cation, notably selected from H<sup>+</sup>, N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> and N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup>.

Application for example for obtaining levitation or self-sustentation systems, as well as for forming contactors or rotating paths.

**11 Claims, No Drawings**

# MAGNETIC FLUIDS AND PROCESS FOR OBTAINING THEM

This invention relates to new magnetic fluids, and to a process for obtaining same. More precisely, the invention relates to new ferrofluids and a process for preparing them.

Ferrofluids are usually defined as being stable colloidal suspensions of ferromagnetic or ferrimagnetic solids. In other words, they are newtonian colloidal suspensions, perfectly stable and fluid in a magnetic field of ferromagnetic or ferrimagnetic subdomains, and therefore they should not be confused with the fluids used in magnetic clutches, which flocculate and lose their fluid character as soon as they are subjected to a magnetic field.

Another type of magnetic fluids is also known, these are paramagnetic aqueous solutions; these solutions contain paramagnetic ions, that is to say, ions with an electronic structure containing unpaired electrons and whose paramagnetism is easily calculated from the quantum numbers characterizing these ions.

However, a magnetic field exerts on a ferrofluid a force approximately twice as great as that the same field exerts on such a paramagnetic solution.

Therefore, ferrofluids have been found to be particularly advantageous as they make it possible to obtain high expulsive forces with a weak magnetic field and, hence, a moderate consumption of energy, to the extent that, for some applications, permanent magnets are sufficient.

The first ferrofluids were made in the laboratories of the NASA round about 1963 (see U.S. Pat. No. 3,215,572) by grinding ferrite for several weeks in the presence of kerosene or oleic acid. But grinding must be continued for a very long time for the solid particles to be small enough (in practice in the range of  $100 \times 10^{-10}$  m) to permit stabilization of the suspension by brownian movement. This corresponds to particles each of which consists of a magnetic subdomain and of only about  $10^5$  atoms. It is the oleic acid which, being adsorbed on the surface of the particles in an organic medium, in particular in kerosene, provides repulsive forces as far as at some tens of Angströms and thus prevents magnetic flocculation.

Such a process is obviously very expensive.

A decisive step for reducing this cost was taken in 1975 by Khalafalla S. E. (see Magnetic Fluids, Chemical Technology Vol. 5 September 1975, pages 540-546, which is incorporated herein by reference) who proposed forming particles of colloidal magnetite by germination and development starting with Fe(II) and Fe(III) (in practice, ferrous chloride and ferric chloride), under suitable conditions of stirring and supersaturation to limit the size of the crystals formed. (See also IBM Technical Disclosure Bulletin, Vol. 19 No. 7, December 1976, pages 2753-2759, which is incorporated herein by reference). The reaction is then conducted in the presence of ammonia, kerosene and oleic acid. The principle of the method was, moreover, previously known by physicians specialized in magnetism under the name of the Elmore method.

In another connection, in France, Papirer E. elaborated a preparation of ferrofluids containing metallic cobalt in suspension in toluene (see "Préparation de suspensions de particules de cobalt finement divisées",

C. R. Acad. Sc. Paris, t.285 (July 18, 1977)- Series C, 77-76).

However, these procedures had the common drawback of necessitating expensive and polluting organic solvents, and/or at least requiring the incorporation of at least one surfactant which may also be a polluting element and which increases the cost of the preparations containing it.

It has now unexpectedly been found that it is possible to obtain ferrofluids without the addition of a surfactant and in water, and it has also been found that the range of ferrofluids which may be prepared in this way is not limited to the case of iron [Fe(III)/Fe(II)] and can comprise other metals to replace Fe(II).

The first object of the invention is new ferrofluids, essentially consisting of an aqueous solution or sol of polyoxoanions of Fe(III) and at least one metal at the oxidation degree II, selected from metals of the first series of transition metals, and notably from Fe(II), Co(II), Mn(II), Cu(II) and Ni(II), with an associated cation. As metal M(II) with oxidation degree II, Fe(II), Co(II) and Cu(II) are especially preferred.

The solubility of the ferrofluid in water depends on the pH, the metal (or metals) M(II) present, the ratio Fe(III)/M(II), and the nature of the cation associated with the polyoxoanion.

The associated cation may be selected from  $H^+$ ,  $N(CH_3)_4^+$ ,  $N(C_2H_5)_4^+$  and the like, so long as they render the polyoxoanion more soluble in water than the  $Na^+$ ,  $K^+$  and  $NH_4^+$  cations, for example. However it should be noted that, when the associated cation is  $H^+$  (i.e. in acidic medium), the polyoxoanion can be regarded, when taken together with the associated cation, as a polycation, and the stability of the solutions also depends on the anions which are in the solution; for example, anions such as  $NO_3^-$ ,  $Cl^-$ ,  $ClO_4^-$  lead to a good stability, whereas  $SO_4^{--}$  precipitates practically quantitatively the polycation.

In each particular case it is possible, using routine trials, for those with an ordinary skill in the art to determine the most suitable pH and the most fitting associated cation.

The new ferrofluids of the invention can be identified by their physical-chemical characteristics as follows:

as stated hereinabove, they consist essentially of an aqueous solution of polyoxoanions of Fe(III) and at least one metal M(II) selected from the first series of transition metals, with an associated cation.

the polyoxoanions form grains with a mean diameter in the order of hundred angströms and having a molecular weight in the order of  $10^6$  to  $10^7$ .

their absorption spectrum in the visible light has a shoulder between about 450 and 500 nm and a maximum absorption at 1400 nm, for Fe(III)/Fe(II), in the near IR.

if necessary, they can be completely dehydrated and resolubilized without difficulty. For example, at  $100^\circ C.$ , dehydration provides a solid comprising one mole water per mole total iron (including, therefore, Fe(II) in the case of Fe(III)/Fe(II)). This solid can be directly resolubilized in water.

the X-ray powder diagram is identical to that of bivalent metal ferrites. In the case of ferrofluid Fe(III)/Fe(II) in particular, even when the iron is completely oxidized, the diagram is not that of  $\gamma Fe_2O_3$ , but remains that of magnetite. Measurement of the width of the lines confirms a size of about 100 angströms for the polyoxoanions.

A second object of the invention is a process for obtaining such ferrofluids, in an aqueous medium and without the addition of a surfactant to prepare them, which process comprises adding to a base of a suitable amount of the product of dissolution in water of the salts of the appropriate metals to form a gel; after optional separation of said gel, effecting a cation exchange by means of an aqueous solution of a suitable cation; and separating the gel so obtained, which is resolubilized to an aqueous solution with, optionally, adjustment of the pH by a base.

In practice, the amount of base to which there is added the dissolution product in water of the metal salts in question is an excess, based on the stoichiometric amount necessary for the formation of hydroxides of the metals present. Depending on the metal M(II) used, heating may be advisable to promote dissolution in the base.

According to another embodiment of this process, it is possible to dispense with gel separation by using a base with a cation suited to form the aforesaid associated cation.

Generally speaking, the sources of the starting metals are salts which can be selected, notably, from:

for Fe(III): ferric alum, ferric chloride and ferric nitrate;

for M(II): Mohr's salt, ferrous chloride, ferrous sulphate and the hydrosoluble salts of metals of oxidation degree II of the first series of transition metals.

Although, in the preparation, the ratio of Fe(III) to the bivalent metal M(II) (whether there be one or more than one of the latter) in the ferrofluid is not critical, a ferrofluid having an initial ratio Fe(III)/M(II) of about 2 is preferable.

It should also be noted that the ratio Fe(III)/M(II) is susceptible to change with time, by the simple fact of oxidation in air, particularly in the case of a ferrofluid of the type Fe(III)/Fe(II). But this is not prejudicial to the qualities of the final product in question.

The strong base initially added to these salts may be any suitable base, and notably NaOH, or again, tetramethyl- or tetraethylammonium hydroxide.

In the particular case of Fe(III)/Fe(II) ferrofluids, it is also possible at this stage to use  $\text{NH}_3$  in aqueous solution. The compound used to provide the associated cation can be selected from suitable acids, notably HCl,  $\text{HNO}_3$  or  $\text{CH}_3\text{COOH}$ , or from tetramethyl- or tetraethylammonium hydroxide.

In each of the steps where a gel is to be collected or recovered, the operation is conducted in the conventional manner, i.e. by decantation on a magnet or by centrifugation, after optional washing with water.

From the magnetic standpoint, the ferrofluids of the invention have characteristics similar to those of ferrofluids hitherto known.

They are, therefore, suited for use in all the applications envisaged for these compounds, bearing in mind that, in the presence of a magnetic field, they constitute an anisotropic medium for which the direction of the field is a preferential direction. These applications are, among others, levitation, self-sustentation or preparation of contactors or rotating paths.

The invention will be described more specifically in the following examples, which in no way limit it.

#### EXAMPLE 1

This example relates to the preparation, according to the invention, of Fe(III)/Fe(II) ferrofluids starting with an initial Fe(III)/Fe(II) ratio of 2.

(a) 400 ml of 0.75 M soda solution was poured into a 2 l beaker and was heated to 100° C. This solution was maintained at 100° C. and was stirred vigorously with a heating magnetic agitator, while a solution formed by mixing 40 ml 1 M  $\text{FeCl}_3$  + 10 ml 2 M  $\text{FeCl}_2$ , 2 M HCl was added, drop by drop (for 5 minutes) from a separating funnel.

(b) The mixture was maintained at about 100° C. for 10 minutes and then left to cool to ambient temperature.

(c) The gel formed was decanted onto a permanent magnet and the supernatant solution was removed with a pipette attached to a water jet aspirator,

(d) The gel recovered in (c) was agitated with 200 ml 1 M nitric acid, for 10 minutes on a magnetic agitator.

Step (c) was then repeated.

(e) Step (d) was repeated twice.

(f) The gel was stirred with 200 ml water for 5 minutes. 200 ml 1 M nitric acid was added and step (c) was repeated.

(g) Step (f) was repeated three times.

(h) The gel was centrifuged at 2000 r.p.m. for 1 hour and the supernatant was removed.

(i) 3 g of this gel were dissolved in water and brought up to a final volume of 10 ml. Determination of total iron and Fe(II) by potassium bichromate in the presence of diphenylamine sulphonate (according to Charlot, *Les Méthodes de Chimie Analytique*; Masson, 1966) demonstrated a total iron concentration of 1.36 M and a ratio Fe(III)/Fe(II)=15.

#### EXAMPLE 2

The procedure according to example 1 was followed except that, instead of step (i), 3 g of the gel of step (h) were dissolved in an aqueous solution of 0.5 M tetramethylammonium hydroxide. Analysis determined the ratio Fe(III)/Fe(II) to be 11.

#### EXAMPLE 3

This example illustrates the preparation, according to the invention, of Fe(III)/Fe(II) ferrofluids from an initial ratio Fe(III)/Fe(II)=5.

The process was conducted as in steps (a) to (h) of the process according to example 1, except that 4 ml 2 M  $\text{FeCl}_2$ , 2 M HCl were used instead of 10 ml in step (a).

The gel obtained in (h) was water soluble and analysis of a solution with a total iron content of 0.68 M demonstrated a ratio Fe(III)/Fe(II) of 20.

#### EXAMPLE 4

40 ml of 1 M  $\text{FeCl}_3$  and 10 ml 2 M  $\text{FeCl}_2$  were mixed with 200 ml water. The mixture was stirred vigorously at ambient temperature and 120 ml of 2 M ammonia was rapidly added. Stirring was continued for 5 minutes.

Then step (c) and the following steps (up to step i) of the process of the invention were followed.

An aqueous ferrofluid was obtained, which was subjected to the following assessments:

the mean charge was determined by means of the analytic method of step (i) according to example 1; the ratio obtained in the Fe(III)/Fe(II) solution was 10. Protometric assessment of this solution by tetramethylammonium revealed a ratio  $\text{H}_3\text{O}^+$ /total iron of 0.07.

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the molar mass was determined by means of measurement of the apparent sedimentation coefficient by analytic ultracentrifugation at 8000 r.p.m. Exploitation of the results, taking as a model a spherical particle, demonstrated a molar mass in the order of  $8 \cdot 10^6$ .

the absorption spectra were established in the visible; these spectra, conducted from 350 nm, showed a shoulder between 450 and 500 nm. Furthermore, a maximum absorption at 1400 nm was revealed in the region close to IR.

#### EXAMPLE 5

40 ml 1 M tetramethylammonium hydroxide were poured onto the mixture of 10 ml 1 M  $\text{FeCl}_3$  and 4 ml 0.5 M  $\text{FeSO}_4$ , 1 N  $\text{H}_2\text{SO}_4$ . The whole was heated until dissolution and the desired ferrofluid was obtained directly.

#### EXAMPLE 6

This example relates to the preparation according to the invention of  $\text{Fe(III)/Co(II)}$  ferrofluids, from an initial ratio iron/cobalt=2.

The process was conducted as in (a) to (h) in example 1, but using 80 ml 0.5 M  $\text{FeCl}_3$  and 40 ml 0.5 M  $\text{Co(NO}_3)_2$ . Determination of cobalt by cerium (IV) in the presence of orthophenanthroline (according to Charlot, *Les Méthodes de Chimie Analytique*; Masson, 1966) in a solution obtained by dissolution of the gel in water, revealed a ratio  $\text{Fe/Co}$  of 1.88. Protometric determination of this same solution with tetramethylammonium enabled the ratio  $\text{H}_3\text{O}^+$ /total iron to be assessed as 0.33.

Furthermore, exploitation of a magnetization curve obtained with this iron-cobalt ferrofluid of a concentration of 0.6 M  $\text{Fe(III)}$ , in an aqueous solution with 0.3 M tetramethylammonium hydroxide enabled the following characteristics to be established:

particle diameter: 121 angströms

standard deviation of size distribution (assumed to be gaussian): 71 angströms

magnetization to saturation of the fluid (1 gauss =  $1 \times 10^{-4}$  teslas): 66 gauss/cm<sup>3</sup>

#### EXAMPLE 7

This example illustrates the preparation, according to the invention, of  $\text{Fe(III)/Co(II)}$  ferrofluids from an initial ratio iron/cobalt=5.

A similar procedure was followed as in example 1 (steps (a) to (c)), but using 100 ml 0.5 M  $\text{FeCl}_3$  and 20 ml 0.5 M  $\text{Co(NO}_3)_2$ . The gel formed and recovered at the end of step (c) was stirred for 10 minutes with 200 ml 4 M acetic acid. Step (c) and subsequently step (h) were repeated. The gel obtained was stirred for 10 minutes with 50 ml 1 M nitric acid.

Step (c) followed by step (h) were again repeated.

Determination of the solution obtained by dissolution in water of the gel recovered showed a ratio iron/cobalt of 4.63 for a concentration (iron)=0.2 M.

#### EXAMPLE 8

This example illustrates the preparation, according to the invention, of  $\text{Fe(III)/Co(II)}$  ferrofluids from an initial ratio iron/cobalt=1.

A similar procedure was followed as in example 1 (steps (a) to (c)) using, this time, 60 ml 0.5 M  $\text{FeCl}_3$  and 60 ml 0.5 M  $\text{Co(NO}_3)_2$ . The gel was recovered and stirred with 200 ml 4 M acetic acid for 10 minutes. Step (c) followed by step (h) were then effected.

Determination of the solution obtained:

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(1) by dissolution of the gel in water, revealed a ratio iron/cobalt of 1.35 for (iron): 0.34 M;

(2) by dissolution of the gel in a 1 M tetramethylammonium hydroxide, revealed a ratio iron/cobalt of 1.32 for (iron)=0.6 M.

What I claim is:

1. Ferrofluids consisting essentially of an aqueous solution free of surfactants of polyoxoanions of  $\text{Fe(III)}$  and at least one metal with an oxidation degree II selected from transition metals consisting of iron, cobalt, manganese, copper and nickel, with an associated cation selected from  $\text{H}^+$ ,  $\text{N(CH}_3)_4^+$  and  $\text{N(C}_2\text{H}_5)_4^+$ .

2. Ferrofluids according to claim 1, wherein the polyoxoanions form particles having a mean diameter in the order of a hundred angströms and a molecular weight in the order of  $10^6$  to  $10^7$ .

3. Ferrofluids according to claim 1 which has an absorption spectrum in the visible light showing a shoulder in the range of about 450 to 500 nm.

4. Ferrofluids according to claim 1, which comprise  $\text{Fe(III)/Fe(II)}$  polyoxoanions and have a maximum absorption at 1400 nm in the near IR.

5. Ferrofluids according to claim 1, which are dehydrated.

6. Ferrofluids according to claim 1, which have an X-ray powder diagram identical to that of bivalent metal ferrites.

7. A process for producing ferrofluids according to claim 1, which comprises adding to a base selected from  $\text{NaOH}$ ,  $\text{NH}_3$  in aqueous solution, tetramethyl ammonium hydroxide and tetraethyl ammonium hydroxide a suitable amount of the product of dissolution in water of the salts of the appropriate metals to form a gel; after optional separation of this gel, effecting on said gel a cation exchange by means of an aqueous solution of a suitable cation provided by means of a compound selected from  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ , tetramethyl ammonium hydroxide and d tetraethyl ammonium; and separating the gel so obtained, which is resolubilized to an aqueous solution with, optionally, adjustment of the pH by a base.

8. A process according to claim 7, wherein amount of the base to which there is added the product of dissolution in water of the metal salts shows an excess based on the stoichiometric amount necessary for the formation of hydroxides of the metals presents.

9. A process according to claim 7, wherein separation of the gel is dispensed with by using a base the cation of which is suited to constitute the associated cation.

10. A process according to claim 7, which comprises using, as sources of starting metals:

for  $\text{Fe(III)}$ : ferric alum, ferric chloride or ferric nitrate;

for  $\text{M(II)}$ : Mohr's salt, ferrous chloride, ferrous sulphate or a hydrosoluble salt of at least one metal of oxidation degree II of said transition metals.

11. Ferrofluids consisting essentially of an aqueous sol free of surfactants of polyoxoanions of  $\text{Fe(III)}$  and at least one metal with an oxidation degree II selected from transition metals consisting of iron, cobalt, manganese, copper and nickel, with an associated cation selected from  $\text{H}^+$ ,  $\text{N(CH}_3)_4^+$  and  $\text{N(C}_2\text{H}_5)_4^+$ , wherein said polyoxoanion particles have a mean diameter in the order of a hundred angströms and a molecular weight in the order of  $10^6$  to  $10^7$ , said ferrofluids having an absorption spectrum in the visible light with a shoulder in the range of about 450 to 500 nm and an X-ray powder diagram identical to that of bivalent metal ferrites.

\* \* \* \* \*



# FINE PARTICLES AND THIN FILMS

## 11.1 INTRODUCTION

When the measured value of some physical or mechanical property is found to depend on the size of the specimen, that property is said to exhibit a *size effect*. Thus the yield stress in tension of an iron whisker 50 microns in diameter is more than a thousand times that of the same iron in the form of a single-crystal rod 1 cm in diameter. On the other hand, both specimens have the same density. In general, only structure-sensitive properties show a size effect.

Among magnetic properties, the saturation magnetization  $M_s$ , for example, is independent of specimen size, but the coercivity  $H_c$  shows a marked size effect. The coercivity of elongated iron particles 150 Å in diameter is some  $10^4$  times that of iron in bulk. In this chapter we will examine some of the magnetic properties of specimens which have been made very small in one dimension (thin films), two dimensions (fine wires), or three dimensions (small particles). Of these, thin films are important in computer applications, and fine particles in permanent magnets. Fine wires are of less importance and will be treated in the last section.

This chapter begins with a discussion of the fundamental properties of fine particles; the more practical aspect of their application in magnets is reserved for Chapter 14. Similarly, the material on thin films is divided mainly between this chapter and Chapter 12, where the mechanism of flux reversal (switching) is described; computer applications are postponed to Chapter 13.

There is an immense literature, both theoretical and experimental, on fine particles and thin films. Fine particles have been reviewed by Paine [11.1], Jacobs and Bean [11.2], and Wohlfarth [11.3, 11.4]. Thin films have been treated in review articles by Goodenough and Smith [11.5], Jacobs and Bean [11.2], Smith [11.6], and Pugh [11.7], and in books by Prutton [G.24] and Soohoo [G.25].

## 11.2 SINGLE-DOMAIN VERSUS MULTI-DOMAIN BEHAVIOR

We have already examined, in Section 9.6, the theoretical reasons for believing that a single crystal will become a single domain when its size is reduced below a critical value  $L_c$  of a few hundred angstroms. What is the experimental evidence for the existence of single-domain particles? There is today a great deal of evidence,

some anisotropies due to shape, for prolate ellipsoids. Shape anisotropy depends on the length/diameter ratio  $l/d$ , but also is proportional to  $M_s$  values shown were calculated for iron ( $M_s = 1714$  emu/cm<sup>3</sup>), and  $\lambda_s$  is taken as typical of many materials.

Examples of anisotropy due to directional order are (a) polycrystalline, annealed 60 Ni-40 Fe (Fig. 10.5), and (b) polycrystalline 50 Ni-50 Fe texture, rolled 55 percent (Fig. 10.12).

and Ni" refers to the uniaxial anisotropy found in polycrystalline nickel longated 2.5 percent (Section 10.6).

entry in the figure shows the anisotropy developed in a single crystal Fe by the treatment described in Section 10.7.

particles were multidomain, and so strained that large microstress led to easy wall motion. To distinguish between these two views, the two specimens, each composed of a very dilute suspension of particles in paraffin wax; in one specimen the particles were smaller than they estimated as 600 Å, and in the other they were larger. (The particles were made dilute to avoid magnetic interactions between particles, and were spherical to eliminate shape anisotropy.) They then measured coercivity, but the field required to saturate the specimen. The results are as follows:

Particle diameter, 200 Å. Field required to saturate, 550 Oe. (Slightly larger than expected for single-domain particles, it is slightly larger. To overcome the crystal anisotropy of nickel, fields of 200–300 Oe are needed, as shown by Fig. 7.2. The presence of a single shape or stress anisotropy can account for the higher field required.)

Particle diameter, 80,000 Å (8 μ). Field required to saturate, such as this field is almost four times the field required to saturate; magnetization mechanism must be entirely different. It is, in fact, appropriate to a multidomain specimen, namely, wall motion. To saturate, the applied field must at least overcome the demagnetizing field, which is  $4\pi M_s/3$  at saturation, where  $4\pi/3$  is the demagnetizing factor of the spherical particles. For nickel,  $4\pi M_s/3$  is  $4\pi(484)/3$  Oe, in good agreement with experiment.

To prove that the 200 Å particles were single domains. Otherwise, 2020 Oe would be needed to saturate them. An originally multidomain can be kept in a saturated state only by a field larger than the coercive field; once this field is removed, the magnetostatic energy associated with the domain walls breaks the particle up into domains and reduces  $M_s$  and the coercive field, to some lower value. But a single-domain particle is always saturated (in the sense of being spontaneously magnetized throughout its volume, but not in the sense of having its  $M_s$  vector parallel to an applied field). An applied field does not have to overcome the demagnetizing field in order to rotate  $M_s$ ; in the limit of zero anisotropy, the field required to rotate  $M_s$  is an infinitesimally small field. (A well-pivoted compass needle is a permanent magnet with a demagnetizing field of more than the earth's field, of a few tenths of an oersted, can easily rotate it.) In viewing this experiment it is to focus on the energies involved. Here, whatever its size, must always have a magnetostatic energy

of all "normal" materials. It is not true of a few substances in which anisotropy in which domains of reversed magnetization are nucleated only with great difficulty. See Section 11.5. However, the existence of such substances does not invalidate the main argument above, which is based on the large difference between the fields required to saturate large and small particles.)

Morrish [G.27] describes a different experiment that proves the existence of single-domain particles. The  $M_s H$  loop of a single particle was measured and shown to have the rectangular shape expected for a uniaxial, single domain.

### 11.3 COERCIVITY OF FINE PARTICLES

In magnetic studies on fine particles the single property of most interest is the coercivity, for two reasons: (1) it must be high, at least exceeding a few hundred oersteds, to be of any value for permanent-magnet applications, and (2) it is a quantity which comes quite naturally out of theoretical calculations of the hysteresis loop.

The coercivity of fine particles has a striking dependence on their size. As the particle size is reduced, it is typically found that the coercivity increases, goes through a maximum, and then tends toward zero. This is clearly shown for three different materials in Fig. 11.1; for the other three the maximum in coercivity has not yet been reached. The very large range of the variables should be noted; the coercivities vary over three orders of magnitude and the particle sizes over five; the smallest particles are less than ten unit cells thick, while the largest have a 0.1 mm diameter and would be retained on a 170-mesh screen.

An understanding of the shape of the curves of Fig. 11.1 has come slowly and only after much experimental and theoretical research. It can now be claimed that the magnetic behavior of fine particles is broadly, but not precisely, understood. The main conclusion is that the mechanism by which the magnetization of a particle changes differs from one part of the size range to another, and much of this chapter is devoted to an examination of these different mechanisms. In anticipation of the results of later sections, Fig. 11.2 shows very schematically how the size range is divided, in relation to the variation of coercivity with particle diameter  $D$ . Beginning at large sizes, we can distinguish the following regions:

1. *Multidomain.* Magnetization changes by domain wall motion (Section 11.5). For most, but not all, materials the size dependence of the coercivity is experimentally found to be given approximately by

$$H_c = a + \frac{b}{D}, \quad (11.1)$$

where  $a$  and  $b$  are constants. This relation is only partially understood.

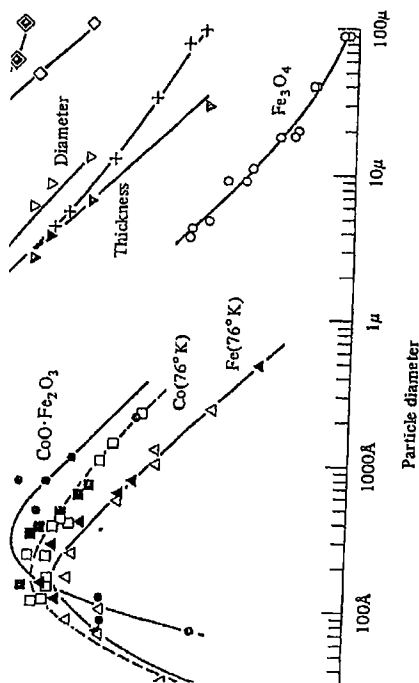


Fig. 11.1 Variation of coercivity  $H_{ci}$  with particle diameter  $D$  (schematic).

studies, the fine magnetic particles must be compacted, with or without a nonmagnetic binder, into a rigid assembly. Then an important variable is the *packing fraction*  $p$ , defined as the volume fraction of magnetic particles in the assembly. The variation of coercivity with  $p$  depends on the kind of anisotropy present. When *shape anisotropy* prevails, the coercivity  $H_{ci}$  decreases as  $p$  increases, because of particle interactions. The following relation has been proposed on theoretical grounds,

$$H_{ci}(p) = H_{ci}(0)(1 - p), \quad (11.3)$$

where  $H_{ci}(0)$  is the coercivity of an isolated particle ( $p = 0$ ), but the underlying theory is not considered sound [11.4]. Some materials obey this relation but many do not. Figure 11.3 shows the behavior of elongated Fe-Co alloy particles having an axial ratio greater than 10 and a diameter of 305 Å.

The nature of the particle-interaction problem is indicated in Fig. 11.4, for elongated single-domain particles. In (a), part of the external field of particle A is sketched, and this field is seen to act in the  $+z$  direction on particle B below it, but in the  $-z$  direction on particle C beside it. Thus the "interaction field" depends not only on the separation of the two particles but also on their positions relative to the magnetization direction of the particle considered as the source of the field. Suppose the  $M_s$  vectors of these particles had all been turned upward by a strong field in the  $+z$  direction. This field is then reduced to zero and increased

$$H_{ci} = g - \frac{h}{D^{3/2}}, \quad (11.2)$$

are constants. This relation is well understood (Section 11.6). At diameter  $D_p$  the coercivity is zero, again because of thermal energy now strong enough to spontaneously demagnetize a previously randomly of particles. Such particles are called *superparamagnetic*

hardness of most fine particles is due to the forces of shape and/or size. In order to study the effect of either of these alone, the experiment to make essentially spherical particles, to eliminate shape effects, elongated particles of a material having low or zero crystal anisotropy, in order to form a practical magnet or a specimen for research

to know, in addition, the field at the interior particle due to all the other particles, both at the start of and during the reversal. As  $p$  increases, the particles come closer together, the interactions become stronger, and the coercivity continues to decrease. Finally, at  $p = 1$ , all particles are everywhere in contact, shape anisotropy is lost, and the coercivity becomes zero, if other forms of anisotropy are absent.

On the other hand, when *crystal anisotropy* prevails, the coercivity is expected to be independent of  $p$ , and this view is supported by experiment. This kind of anisotropy is due to forces (spin-orbit coupling) which are "internal" to the particle and not, like shape anisotropy, to magnetostatic fields external to the particle. At any value of  $p$ , including unity, the crystal anisotropy forces remain constant.

#### 11.4 MAGNETIZATION REVERSAL BY SPIN ROTATION

In Section 9.13 we examined the hysteresis loops of uniaxial single-domain particles reversing their magnetization by rotation, as calculated by Stoner and Wohlfarth [7.23]. The tacit assumption made there was that the spins of all the atoms in the particle remained parallel to one another during the rotation. This mode of reversal is called *coherent rotation*, *rotation in unison*, or the *Stoner-Wohlfarth mode*.

For spherical single-domain particles of iron, with their easy axes aligned with the field, the intrinsic coercivity  $H_{ci}$  due to crystal anisotropy is equal to  $2K/M_s = 2(4.8 \times 10^5)/1714 = 560$  Oe, from Eq. (9.51). Aligned elongated particles, reversing by coherent rotation, have a coercivity due to shape anisotropy given by Eq. (9.49), namely,

$$H_{ci} = (N_a - N_b)M_s, \quad (11.4)$$

where  $N_a$  is the demagnetizing factor along the short axis and  $N_b$  along the long one. The maximum value of  $(N_a - N_b)$  for infinite elongation is  $2\pi$ , so that the maximum attainable coercivity from shape anisotropy is  $2\pi M_s$ . For aligned iron particles we calculated, in Table 9.2, that  $H_{ci}$  should be 10,100 Oe for an axial ratio  $c/a$  of 10 and 10,800 Oe for infinite elongation. About 1955 a method was developed for making very thin, elongated, iron particles with axial ratios from about 1 to well over 10 by electrodeposition on a mercury cathode. (Details of the method are given in Section 14.7.) Measurements on aligned, dilute composites of these particles showed that  $H_{ci}$  increased with  $c/a$  but did not exceed about 1800 Oe for  $c/a$  larger than 10 [11.9]. These results showed that the observed coercivity certainly could not be explained by crystal anisotropy, but neither was it as large as expected for shape anisotropy. In fact, it was only some 18 percent of the theoretical value. This discrepancy forced theoreticians to question the assumption on which Eq. (11.4) is based, namely, coherent rotation of the spins. They therefore examined possible modes of *incoherent* rotation, in which all spins do

Fig. 11.3 Variation of  $H_{ci}$  with  $p$  for elongated Fe-Co particles. After Luborsky [11.9]

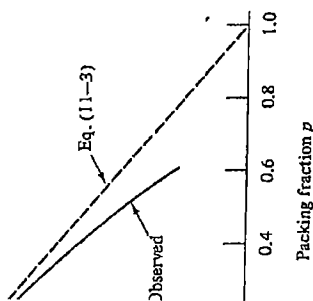
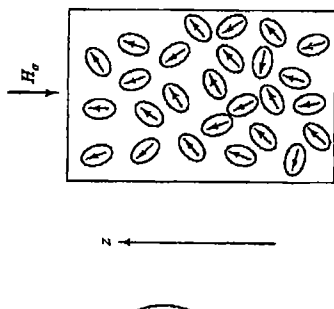
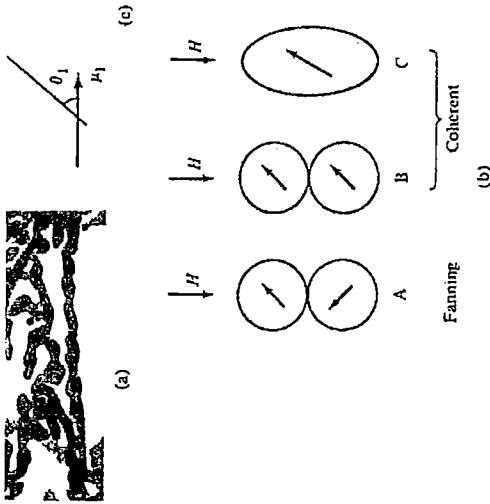


Fig. 11.4 Particle interactions.



m. The field of A at C now aids the applied field, and C would magnetize at a lower applied field than if A were absent; the coercivity would be lowered. The opposite conclusion would be reached only the pair of A and B particles. In either case we have a real problem to deal with. A quantitative study of the interactions is very difficult, and the exact solution of the many-particle problem represented by Fig. 11.4 (b), a cylindrical compact of a large number of particles, is usually impossible. If a reversing field  $H_a$  is applied in the  $-z$



electron micrograph of electrodeposited iron particles [11.9]. (b) Models of reversal modes. (c) Dipole-dipole interactions.

allel, to see if such modes would give coercivities in better accord with the two most important of these incoherent modes are *magnetizing* and *curling*.

suggested by the shape of the electrodeposited iron particles observed in electron microscope. Figure 11.5(a) shows that these particles are not spherical but are characterized by periodic bulges rather than smooth peanut shape, that they can be approximated by the "chain of spheres" model of Bean [11.10] and by the "chain of spheres" model of Bean [11.10] possible reversal mechanisms: (1) symmetric fanning (A), in which successive spheres in the chain fan out in a plane by rotating about a common axis, and (2) coherent rotation (B) in which all the spheres are always parallel. The coercivities calculated for these two mechanisms were then compared with that calculated for coherent rotation (C) of the same axial ratio as the chain of spheres.

$$E_{ms} = \frac{\mu_1 \mu_2}{r^3} [\cos(\theta_1 - \theta_2) - 3 \cos \theta_1 \cos \theta_2], \quad (11.5)$$

where  $r$  is their distance apart and  $\theta_1$  and  $\theta_2$  are defined in Fig. 11.5(c). For a two-sphere chain reversing by fanning,  $\mu_1 = \mu_2 = \mu$ ,  $r = a$ ,  $\theta_1 = \theta$ ,  $\theta_2 = -\theta$ , and Eq. (11.5) reduces to

$$\text{(fanning, A)} \quad E_{ms} = -\frac{\mu^2}{a^3} (1 + \cos^2 \theta). \quad (11.6)$$

This energy depends on  $\theta$  in exactly the same way as the various forms of uniaxial anisotropy energy we have previously encountered. The magnetostatic coupling between two dipoles therefore causes the pair to have a uniaxial anisotropy with an easy axis along the line joining the dipoles. This has been called *interaction anisotropy*.

(In the fanning mode, the spins in one sphere are not parallel to those in the adjacent sphere at the point of contact. Some exchange energy is therefore introduced. But exchange energy is essentially short range, which means that the spins contributing to this energy in the fanning mode form only a small fraction of the total. Thus the total exchange energy is considered to be small, and it can be made still smaller by imagining the spheres to be slightly separated. It is neglected in these calculations.)

To find the coercivity of the two-sphere chain in a field  $H$  parallel to the chain axis, we note that the potential energy  $E_p$  in the field is  $2\mu H \cos \theta$ , when  $H$  is antiparallel to  $\mu$ . The total energy is then

$$E = E_{ms} + E_p = -\frac{\mu^2}{a^3} (1 + \cos^2 \theta) + 2 \mu H \cos \theta. \quad (11.7)$$

This equation is of the same form as Eq. (9.40) for a uniaxial particle reversing coherently. Therefore, a fanning reversal is also characterized by a rectangular hysteresis loop, and the coercivity is the field at which the moments will flip from  $\theta = 0$  to  $\theta = 180^\circ$ . To find it we set  $d^2 E/d\theta^2$  equal to zero and proceed in exactly the same way as in Section 9.13. The result, for the intrinsic coercivity, is

$$\text{(fanning, A)} \quad H_c = \frac{\mu}{a^3} = \frac{\pi M_s}{6}, \quad (11.8)$$

because  $\mu = (M_s/4\pi/3)(a/2)^3$ .

For a two-sphere chain rotating coherently (B),  $\theta_1 = \theta_2 = \theta$ , with the result that

$$\text{(coherent, B)} \quad E_{ms} = \frac{\mu^2}{a^3} (1 - 3 \cos^2 \theta). \quad (11.9)$$

# Ferromagnetism

Iron, nickel, cobalt and some of the rare earths (gadolinium, dysprosium) exhibit a unique magnetic behavior which is called ferromagnetism because iron (ferrum in Latin) is the most common and most dramatic example. Samarium and neodymium in alloys with cobalt have been used to fabricate very strong rare-earth magnets.

Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired electron spins to line up parallel with each other in a region called a domain. Within the domain, the magnetic field is intense, but in a bulk sample the material will usually be unmagnetized because the many domains will themselves be randomly oriented with respect to one another. Ferromagnetism manifests itself in the fact that a small externally imposed magnetic field, say from a solenoid, can cause the magnetic domains to line up with each other and the material is said to be magnetized. The driving magnetic field will then be increased by a large factor which is usually expressed as a relative permeability for the material. There are many practical applications of ferromagnetic materials, such as the electromagnet.

Ferromagnets will tend to stay magnetized to some extent after being subjected to an external magnetic field. This tendency to "remember their magnetic history" is called hysteresis. The fraction of the saturation magnetization which is retained when the driving field is removed is called the remanence of the material, and is an important factor in permanent magnets.

All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. This temperature is called the Curie temperature.

Ferromagnetic materials will respond mechanically to an impressed magnetic field, changing length slightly in the direction of the applied field. This property, called magnetostriction, leads to the familiar hum of transformers as they respond mechanically to 60 Hz AC voltages.

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## Long Range Order in Ferromagnets

The long range order which creates magnetic domains in ferromagnetic materials arises from a quantum mechanical interaction at the atomic level. This interaction is remarkable in that it locks the magnetic moments of neighboring atoms into a rigid parallel order over a large number of atoms in spite of the thermal agitation which tends to randomize any atomic-level order. Sizes of domains range from a 0.1 mm to a few mm. When an external magnetic field is applied, the domains already aligned in the direction of this field grow at the expense of their neighbors. If all the spins were aligned in a piece of iron, the field would be about 2.1 Tesla. A magnetic field of about 1 T can be produced in annealed iron with an external field of about 0.0002 T, a multiplication of the external field by a factor of 5000! For a given ferromagnetic material the long range order abruptly disappears at a certain temperature which is called the Curie temperature for the material. The Curie temperature of iron is about 1043 K.

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## The Curie Temperature

For a given ferromagnetic material the long range order abruptly disappears at a certain temperature which is called the Curie temperature for the material. The Curie temperature of iron is about 1043 K. The Curie temperature gives an idea of the amount of energy takes to break up the long-range ordering in the material. At 1043 K the thermal energy is about 0.135 eV compared to about 0.04 eV at room temperature.

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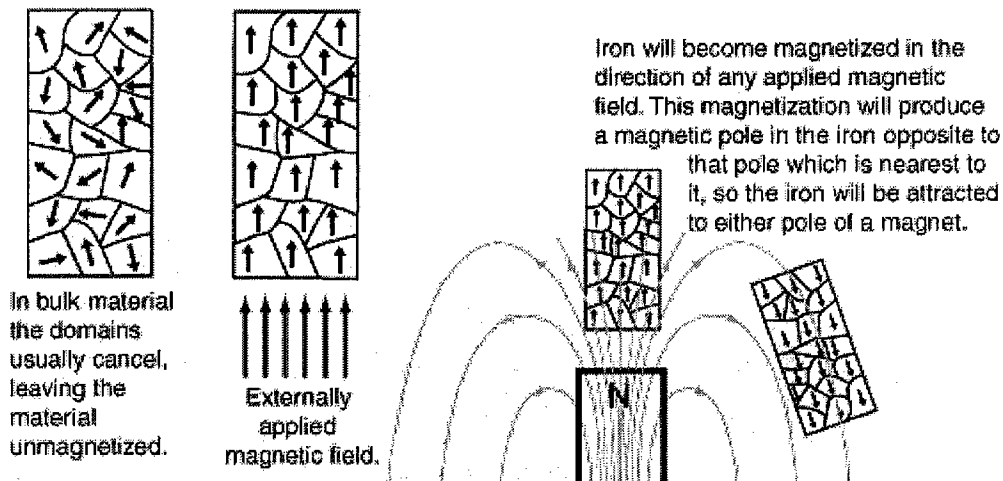
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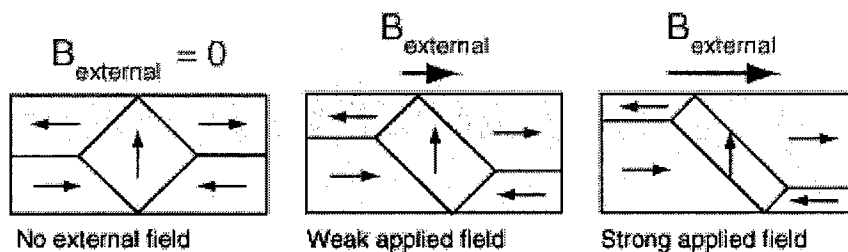
## Magnetic Domains

The microscopic ordering of electron spins characteristic of ferromagnetic materials leads to the formation of regions of magnetic alignment called domains.



The main implication of the domains is that there is already a high degree of magnetization in ferromagnetic materials within individual domains, but that in the absence of external magnetic fields those domains are randomly oriented. A modest applied magnetic field can cause a larger degree of alignment of the magnetic moments with the external field, giving a large multiplication of the applied field.

These illustrations of domains are conceptual only and not meant to give an accurate scale of the size or shape of domains. The microscopic evidence about magnetization indicates that the net magnetization of ferromagnetic materials in response to an external magnetic field may actually occur more by the growth of the domains parallel to the applied field at the expense of other domains rather than the reorientation of the domains themselves as implied in the sketch.



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Some of the more direct evidence we have about domains comes from imaging of domains in single crystals of ferromagnetic materials. The sketches above are after Young and are adapted from magnified images of domain boundaries in single crystals of nickel. They suggest that the effect of external magnetic fields is to cause the domain boundaries to shift in favor of those domains which are parallel to the applied field. It is not clear how this applies to bulk magnetic materials which are polycrystalline. Keep in mind the fact that the internal magnetic fields which come from the long range ordering of the electron spins are much stronger, sometimes hundreds of times stronger, than the external magnetic fields required to produce these changes in domain alignment. The effective multiplication of the external field which can be achieved by the alignment of the domains is often expressed in terms of the relative permeability.

Domains may be made visible with the use of magnetic colloidal suspensions which concentrate along the domain boundaries. The domain boundaries can be imaged by polarized light, and also with the use of electron diffraction. Observation of domain boundary movement under the influence of applied magnetic fields has aided in the development of theoretical treatments. It has been demonstrated that the formation of domains minimizes the magnetic contribution to the free energy.

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## Relative Permeability

The magnetic constant  $\mu_0 = 4\pi \times 10^{-7} \text{ T m/A}$  is called the permeability of space. The permeabilities of most materials are very close to  $\mu_0$  since most materials will be classified as either paramagnetic or diamagnetic. But in ferromagnetic materials the permeability may be very large and it is convenient to characterize the materials by a relative permeability.

Some representative relative permeabilities:

magnetic iron .....	200	
nickel .....	100	
permalloy.....	8,000	at a magnetic flux density of 0.002 W/m <sup>2</sup>
(78.5% nickel, 21.5% iron)		
mumetal.....	20,000	
(75% nickel, 2% chromium, 5% copper, 18% iron)		

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When ferromagnetic materials are used in applications like an iron-core solenoid, the relative permeability gives you an idea of the kind of multiplication of the applied magnetic field that can be achieved by having the ferromagnetic core present. So for an ordinary iron core you might expect a magnification of about 200 compared to the magnetic field produced by the solenoid current with just an air core. This statement has exceptions and limits, since you do reach a saturation magnetization of the iron core quickly, as illustrated in the discussion of hysteresis.

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## Applications of Ferromagnetism

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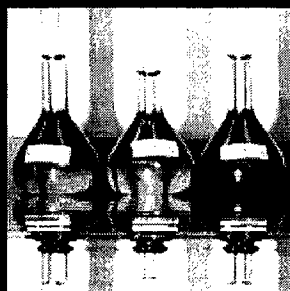
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## Meito Sangyo Co., Ltd.

### FINE CHEMICALS DIVISION

Welcome to our "web" catalogue.

#### Feature

By using of fermentation technology from microorganism, Meito Sangyo Co., Ltd. Fine chemicals Division produces unique products, such as polysaccharide and enzymes.

Out of our products, both dextran used for a plasma expander and microbial rennet, cheese production enzyme are produced by limited manufacturers worldwide.

Dextran derivatives with a variety of functional group can be produced from Dextran by chemical reaction. Anion-donating reaction such as sulphonation, carboxymethylation or cation-donating reaction like tertiary amination can be carried out for purpose-made product. Since dextran acts as a protective colloid to keep solution highly dispersed, iron oxide or magnetic iron oxide dextran complex can be also manufactured. These resultant products are physiological and biocompatible ones which are applicable as raw materials for pharmaceuticals and cosmetics.

Especially in Japan, Meito Sangyo is sole manufacturer of these products.

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Our Hachioji factory where we are producing Dextran products and lipases has established the environmental management system conforming to ISO14001, which is the international environmental management standard, and was granted ISO14001 Certificate of Registration in June 2001. Our registered site is now working on continual improvements in our performance to achieve the environmental objects and targets according to our environmental policy.

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